Transport and Sedimentation of Pollutants in a River Reach: A Chemical Mass Balance Approach

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The River Höje in the south of Sweden is a typical receiving water for urban and rural runoff. Mass balance calculations over a 17-month period indicate that pollutants are retained in the sediments of the investigated 5-km-long reach of the stream (90 tons of biochemical oxygen demand (BOD_7), 850 tons of chloride, 2.1 tons of copper, 3.2 tons of zinc, and 1.0 ton of lead). Other pollutants such as suspended solids and phosphorus appear to be both retained and washed-out, depending on loading rates and local stream conditions. The retained pollutants represent a substantial part of the total mass transport through the stream (14–47%). Almost half of the transported zinc is retained within the stream sediment. Subsequently, the deposited pollutants represent a potential pollution source. Analyses of sediment samples verify that the upper sediments contain high concentrations of heavy metals.

INTRODUCTION

Studies on in-stream reactions and sediment dynamics have received increased attention during recent years. There are several reasons for this. Because of substantial efforts to reduce point pollution sources the relative effect of nonpoint pollution has increased [*Latimer et al.*, 1988; *Elder*, 1985]. This has increased the need to identify major sources of nutrients and trace elements deposited within the river system. The increasing environmental problems due to acidification and metal contamination of streams have also required a more fundamental understanding of sediment dynamics and pathways for dissolved and particulate metal transport [*Bencala et al.*, 1984; *Moriarty and Hanson*, 1988; *Salomons and Förstner*, 1984].

A commonly used approach to study in-stream reactions, deposition, erosion, or resuspension is chemical mass balances [*Yuretich and Batchelder*, 1988; *Katz et al.*, 1985; *Paces*, 1985; *Christophersen and Wright*, 1981; *Plummer and Back*, 1980]. This approach may be useful when dynamic and highly variable relationships between physical and chemical mechanisms on a larger scale within a given reach of a river must be understood.

This paper presents detailed water budgets and mass balances of water quality constituents such as suspended solids, chloride, biochemical oxygen demand, phosphorus, copper, zinc, and lead for a 5-km-long river reach in the south of Sweden. The objective of the study was to examine transport and sedimentation of the above constituents. For this purpose, continuous water level recordings and weekly flow-proportional water quality samples were collected over a 17-month period (May 1978–September 1979; *Hogland and Niemczynowicz* [1979, 1980]).

AREA DESCRIPTION

Water budgets and chemical mass balances were established for a 5-km-long reach of the River Höje close to the city of Lund (Figure 1). This reach receives both storm water and treated wastewater from the city, which has about

65,000 inhabitants. Storm water from separate sewers draining a total of 8.45 km^2 is discharged at four points to this reach of the river (D1, 4.40 km^2; D2, 0.45 km^2; D3, 0.50 km^2; and D11 3.10 km^2; see Figure 1). The central parts of the city are drained by a combined sewer system covering 8.40 km^2 [*Hogland*, 1986; *Niemczynowicz*, 1984]. The water from this area is led to the treatment plant where water is treated mechanically, chemically, and biologically. During heavy rainfall, combined sewer overflow may, however, discharge directly into the stream through the D2 and D11 outlets or from two detention basins close to the treatment plant outlet (T station). The mean impervious part of the total area (16.85 km^2) contributing to the river reach is about 30%.

The River Höje basin contains small towns and villages surrounded by agricultural areas (Figure 1). The total catchment area is about 310 km^2. About 250 km^2 is drained through the discharge point at the city of Lund. The population in the catchment is about 80,000 persons. The land use within the area can be divided into agricultural (59%), forest (18%), urban (12%), meadows (10%), and lakes (<1%) [*Hogland*, 1986; *Hogland and Berndtsson*, 1983]. The soil types of the area are mainly sandy loam and moraine with spots of fine and coarse sediments. The quantity and quality of the stream water is affected by discharge from urban areas but also by extensive drainage from agricultural areas and forests.

METHODS

The study reported herein consists of some of the results from an extensive data collection program aiming at establishing complete water and chemical mass balances for the city of Lund [*Hogland and Niemczynowicz*, 1979, 1980; *Hogland*, 1986]. The urban data collection program was also supplemented by extensive hydrological observations in a small experimental field research basin located just outside the city of Lund [e.g., *Zhang and Berndtsson*, 1988, also manuscript in preparation, 1990].

The river water level was measured at the receiving water stations (R1, R2, and R3) by mechanical water level gages and through stage-discharge relationships converted to flow. At each of the stormwater outlets (D1, D2, D3, and D11),
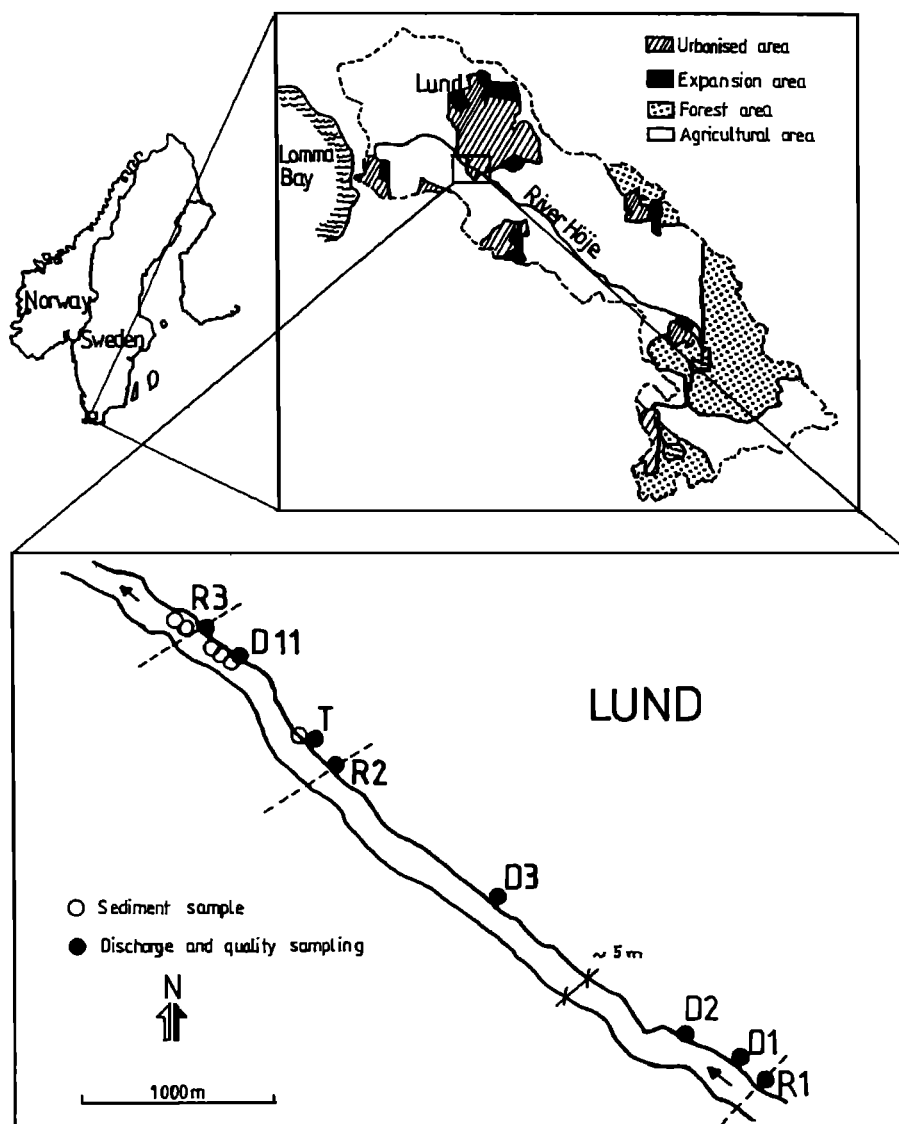
Fig 1.   Sampling sites at the River Höje; D stations are storm water outlets, R stations are receiving water sites, and the
T station is the outlet from the treatment plant (the entire River Höje basin and general location are shown in insets).

dams with sharp-crested weirs were constructed. The water level was measured by a dual system of a mechanical water level gage and an air bubble water level gage. For each weir, stage-discharge relationships were established. Treated wastewater discharge was measured continuously at the treatment plant (T station). Precipitation and standard meteorological and hydrological variables were measured both in an urban observation station and in the nearby experimental field research basin. Rainfall was also measured at 12 automatic stations by use of tipping buckets [*Niemczynow-icz*, 1984].

Water quality samples were taken by use of automatic flow-proportional sampling at storm water and receiving water stations (D1, D2, D3, D11, R1, R2, and R3) and collected in polyethylene bottles. Water samples were taken from the upper 50 cm of the water surfaces. Before sampling, the sampling equipment at each station was automatically rinsed with river water. The polyethylene containers were repeatedly prerinsed with organic solvents (free from phosphorus) and acid-leached (chromic-sulphuric acid followed by distilled water). Treated wastewater was sampled by

hand at two points, three times a week and after major rainfall events. All water quality samples were collected three times a week and put in a freezer. Before analysis the flow-proportional samples were thawed and mixed into a weekly mean sample (the flow-proportional samples were mixed and a homogeneous sample for analyses was taken out).

In addition to the water quality samples taken in the stream and at discharge points to the stream, different types of samples were taken on a more or less simultaneous basis. Concurrent with the runoff sampling, total atmospheric fallout was measured on a monthly basis at 12 stations evenly distributed over the city of Lund. Discrete sampling of melting snow discharge and snow quality was made during the winter period. Similar measurements were also made for storm water quality and combined sewer overflow quality at different points upstream in the sewer system [*Hogland*, 1986].

Suspended solids, biochemical oxygen demand (BOD_7), and chloride were analyzed according to standard methods (Swedish standards SIS028112, SS928113, SS028120, and

SIS028120, respectively). Suspended solids were determined by filtration of a well-mixed sample on a standard glass-fiber filter disk (0.45 μm filter; detection limit SS = <5 mg/L). BOD_7 was determined over 7 days for biochemical oxidation of organic substances at 20°C. $C_4H_8N_2S$ was added in order to prevent nitrification [Young, 1973]. The detection limit for BOD_7 is about 5 mg/L. Chloride content was measured by titration with mercuric nitrate solution (see American Public Health Association (APHA) [1975]; detection limit = 10 mg/L). Total phosphorus was analyzed according to APHA [1975] (detection limit = 0.01 mg/L).

Water samples for metal analyses were filtered through a standard type 0.45-μm pore diameter membrane filter. The samples were then preserved by acidifying with concentrated HNO_3 to pH = 2 [e.g., APHA, 1975]. Metals were analyzed by use of atomic absorption spectrophotometry (Perkin Elmer 303). Consequently, the results represent filtrable (dissolved) metals. Quantification of the metals was based upon calibration curves of standard solutions of metals. These calibration curves were determined every time before analysis of water samples (approximate detection limits for Cu = <0.01 mg/L; Zn = <0.01 mg/L; Pb = <0.05 mg/L).

The results of the mass balance calculations were compared with metal analyses of sediment samples taken in August 1989. The sediment samples were placed in a freezer immediately after sampling. After thawing and drying (105°C) the samples were digested by 7 M HNO_3 (digestion in closed teflon containers and by use of microwave ovens) and then filtered before analysis by use of inductively coupled plasma mass spectrometry.

Water budgets and chemical mass balances were calculated for the 5-km-long river reach in order to study accumulation and wash-out tendencies. This was done by adding observed inflows to the 5-km reach and subtracting observed outflows. Initial water budgets were calculated by adding discharge at the upstream receiving water station (R1 station), all storm water stations (D1, D2, D3, and D11), and the treated wastewater station (T station), and subtracting the discharge from the outflow-receiving water station (R3 station). This resulted in a net deficit (outflow exceeded inflow) in the annual water balance of 6200 × 10^3 m^3 (9% of the observed total inflow to the river reach), which indicated that 9% of the total inflow to the 5-km reach is drained from various kinds of unknown sources. When examining the weekly water budgets, however, it appeared that main deficits arose during 3 weeks in March and April (during the snowmelt). The winter in 1978/1979 was unusual in the sense that large amounts of snow accumulated during January and February but melted rapidly during a few weeks. The main unknown inflow to the river reach during this period consists mostly of melting water from snow and ice, which appears as surface runoff on the frozen topsoil. Thus it was decided to correct initial water budgets for this type of nonpoint inflow source by calculating the surface runoff due to melting snow on the basis of contributing areas, available snowpack and water content, and temperature, according to observations performed during the same period [Hogland, 1986]. Similar corrections were made for direct precipitation on the water surface of the stream and for evaporation from the free water surface. These corrections decreased the annual water budget deficit at the R3 station from about 6200 × 10^3 m^3 to 500 × 10^3 m^3 (from 9 to less than 1% of the total annual inflow).

This indicates that it has been possible to estimate major inflow and outflow components to the reach.

The initial chemical mass balances were also corrected similarly by adding mass transport according to mean concentrations of discrete sampling of snowmelt surface runoff during the same period [Hogland, 1986]. Precipitation was also considered to contribute to the chemical mass balances according to observed atmospheric fallout. These corrections did not, however, alter the chemical mass balances significantly.

QUALITY-DISCHARGE RELATIONSHIPS

Time series of water quality constituents at the inflow and outflow receiving water stations are shown in Figure 2 (R1 and R3). Table 1 shows the mean, median, and standard deviations for the corresponding samples [Hogland, 1986]. The discharge in the river varies from about 0.1 m^3/s in the late summer to about 15.0 m^3/s during the snowmelt in March or April (R3 station downstream of Lund).

The urban storm water and the treated wastewater discharge represent a substantial part of the river flow. The mean discharge from the treatment plant is about 0.5 m^3/s but may increase up to more than 1.0 m^3/s during snowmelt. Consequently, the urban storm water and the treated wastewater represent major pollution inputs to the river. In fact, the treated wastewater discharge usually represents 30–50% (during low-flow periods the treated wastewater may constitute the bulk discharge) and the storm water discharge 5–10% of the natural river discharge [Hogland, 1986]. From Figure 2, however, it is seen that in spite of the large impact from treated wastewater and urban storm water discharge, the upstream and downstream stations mainly follow the same time patterns for water quality concentrations. As is seen from Table 1, copper and lead even have a somewhat lower concentration downstream of Lund as compared to the upstream values. This may imply a certain retention within the system but may also be a simple dilution effect caused by the storm water.

The various water quality constituents follow different time patterns over the year. The most obvious seasonal pattern is displayed by biological oxygen demand with elevated concentrations during the spring and summer period and lower concentrations during late autumn and winter. This annual cycle is natural considering the increased biological activity during the warm season. Chloride concentrations also seem to display a seasonal behavior (Figure 2). The elevated chloride concentrations during the winter period are caused by deicing practices. It has been estimated that about 2500 × 10^3 kg NaCl was spread on streets and impermeable areas in Lund during the winter 1978/1979 [Hogland, 1979]. The effect of this is clearly seen in Figure 2 as peak values during weeks 50–12 (especially the elevated concentrations at the R3 station). However, elevated chloride concentrations are also occurring during the summer period (weeks 24–38). In spite of the high concentrations, a similar elevation in mass transport is not observed (Figure 4). The high summer concentrations may therefore be an effect of low natural stream flow in relation to a comparatively high discharge of treated wastewater.

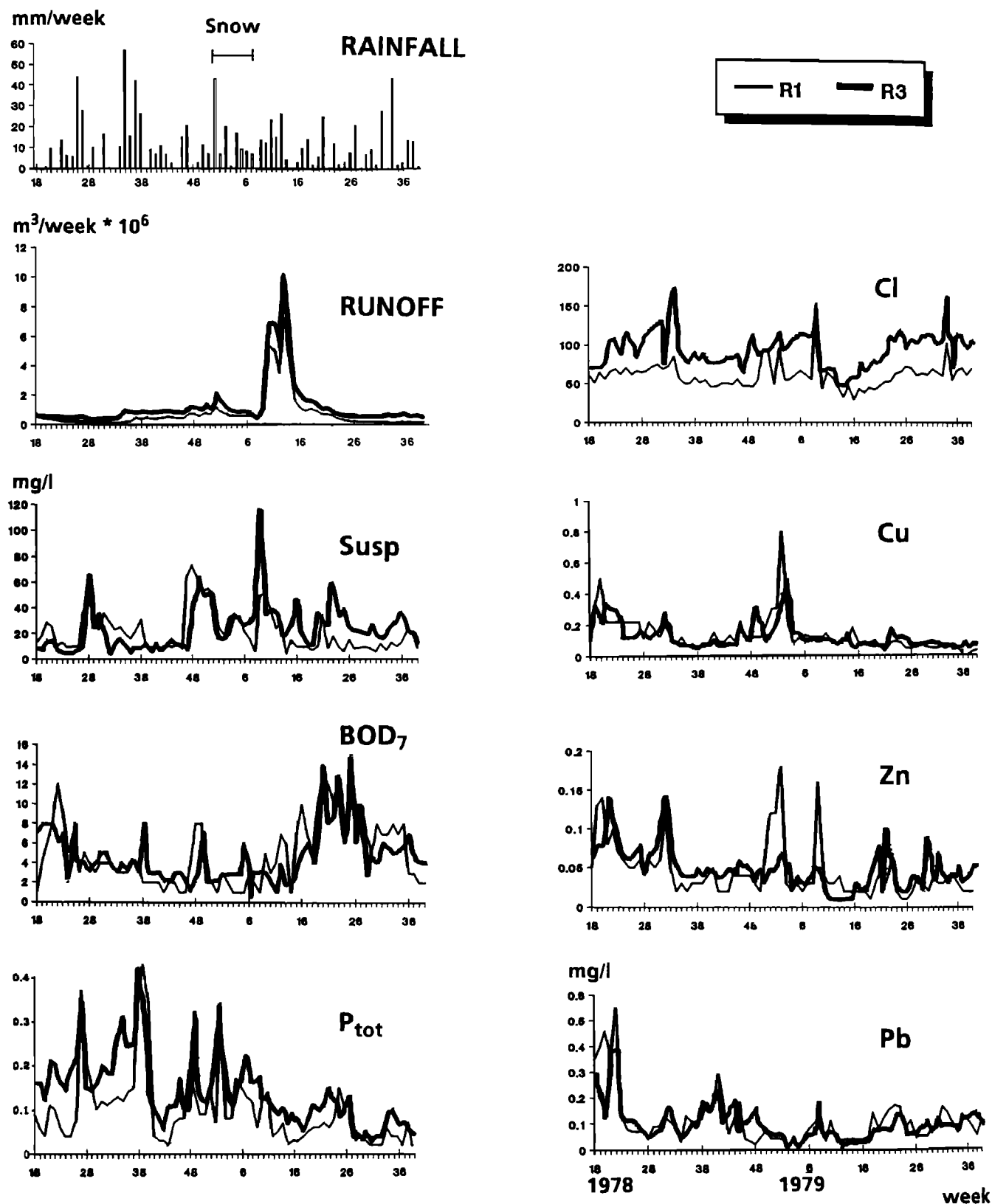The different water quality parameters display different

Fig 2.   Time series of weekly discharge and weekly water quality samples at the inflow and outflow receiving water stations (R1 and R3 stations).

interdependence. Copper, zinc, and lead concentrations are correlated. This is seen in the correlation matrix for concentrations of all parameters (Table 2).

The discharge dependence of the stream chemistry is

shown in Figure 3 (receiving water stations R1, R2, and R3). All parameters display a more or less exponential behavior toward the flow rate which is expected [e.g., *Feller and Kimmins*, 1979; *Verry*, 1975]. Some of the parameters (sus-

TABLE 1. Statistical Properties of Weekly Water Quality Samples at the Inflow and Outflow Receiving Water Stations

	R1			R3		
	Mean	Median	Standard Deviation	Mean	Median	Standard Deviation
pH	7.9	7.9	0.5	7.6	7.6	0.4
SS, mg/L	21.5	15.5	16.0	24.0	21.0	18.0
BOD_7, mg/L	4.90	4.00	3.25	5.15	4.00	4.10
P_{tot}, mg/L	0.10	0.08	0.08	0.14	0.13	0.08
Cl, mg/L	60.5	60.0	17.0	94.0	92.0	23.5
Cu, mg/L	0.130	0.095	0.115	0.115	0.080	0.090
Zn, mg/L	0.045	0.030	0.035	0.065	0.050	0.130
Pb, mg/L	0.110	0.080	0.100	0.100	0.080	0.070

At each station there are 74 samples.

pended solids and BOD_7), however, display most of the data near the origin.

MASS TRANSPORT

Figure 4 shows the chemical mass transport at stations R1 and R3. The major mass transport occurs during snowmelt (Figure 2). For suspended solids, BOD_7, and P_{tot} there are mainly one or two major mass transport events, which seem to follow the general runoff pattern. For metals (copper, zinc, and lead), however, there are three or more such events, which are not connected to major runoff events. This indicates that metal transport is not only related to discharge.

CHEMICAL MASS BALANCES

Figure 5 shows the accumulated weekly deviations of water budgets and chemical mass balances. The accumulated deviations of water budgets display a typical annual cycle. It is seen that the May–July period (weeks 18–30) represents a period when water is lost from the reach (continuous accumulation). This period is followed by a period when water is drained from the surroundings to the stream (continuous negative balances during the weeks 31–4). The spring period again means that water is lost from the reach to the surroundings.

The sinusoidal behavior of accumulated deviations of the water budgets reflects the annual variation of the groundwater to the river. The groundwater table was observed in 21

TABLE 2. Correlation Matrix for Pairwise Combined Weekly Water Quality Samples at the Receiving Water Stations

	SS	BOD_7	P_{tot}	Cl	Cu	Zn	Pb
SS	1	0.194	0.155	0.138	0.043	0.036	−0.256
BOD_7		1	−0.010	0.053	−0.071	0.115	0.146
P_{tot}			1	0.158	0.376*	0.218	0.075
Cl				1	0.094	0.284*	0.002
Cu					1	0.568*	0.194
Zn						1	0.434*
Pb							1

Receiving water stations are R1, R2, and R3; number of samples is 74; and correlation coefficients are expressed as means of the three stations.
Values are statistically significant at 0.01 rejection level [Yevjevich, 1972].

open wells (shallow groundwater) and 4 deep observation tubes (deep groundwater) at different distances from the investigated river reach [Lindh, 1983]. The depth to the groundwater table in the open wells typically varied between a maximum (3–5 m) in summer to a minimum (1–2 m) in winter. That is, an inverse relationship exists between the accumulated water balance in Figure 5 and the groundwater table fluctuations. This indicates that when the groundwater table is low, river water is lost to the groundwater system (inflow exceeds outflow in Figure 5). In the same way, when the groundwater table is high, groundwater is drained by the river (outflow exceeds inflow in Figure 5). It is seen that about 1% of the annual river flow is lost to the groundwater during spring and early summer. Approximately the same amount of water is drained from the groundwater to the river during autumn and early winter.

Figure 5 shows the accumulated deviations in the chemical mass balances for the reaches of the stream (R1-R3, R1-R2, and R2-R3). By comparing the graph for the R1-R2 reach and the R2-R3 reach, respectively, the influence of the load from the treated wastewater outlet is displayed. The graph for the R1-R3 reach gives the total accumulated deviations. A continuous accumulation occurs for most of the constituents. Exceptions from this general pattern are suspended solids, phosphorus, BOD_7, and lead. Suspended solids, phosphorus, and BOD_7 display large differences between the two reaches R1-R2 and R2-R3. Suspended solids, phosphorus, and BOD_7 are continuously accumulated in the R2-R3 reach, probably influenced by discharge from the wastewater treatment plant. In the upstream reach (R1-R2), however, a continuous wash-out of suspended solids and phosphorus seem to occur. Lead displays the most pronounced seasonal behavior, similar to that of the accumulated deviations of the water budgets.

Table 3 shows the total accumulation and accumulation depending on reach. The relation between the total accumulation and total mass flux into the reach is also given. It is seen that the accumulation in most cases is a substantial part of the total mass flux. For zinc, nearly half of the total mass transport (47%) seems to be retained in the stream. The table also shows the accumulation depending on reach.

SEDIMENT SAMPLING

In order to verify sediment retention of pollutants and approximately show the order or magnitude of the accumu-
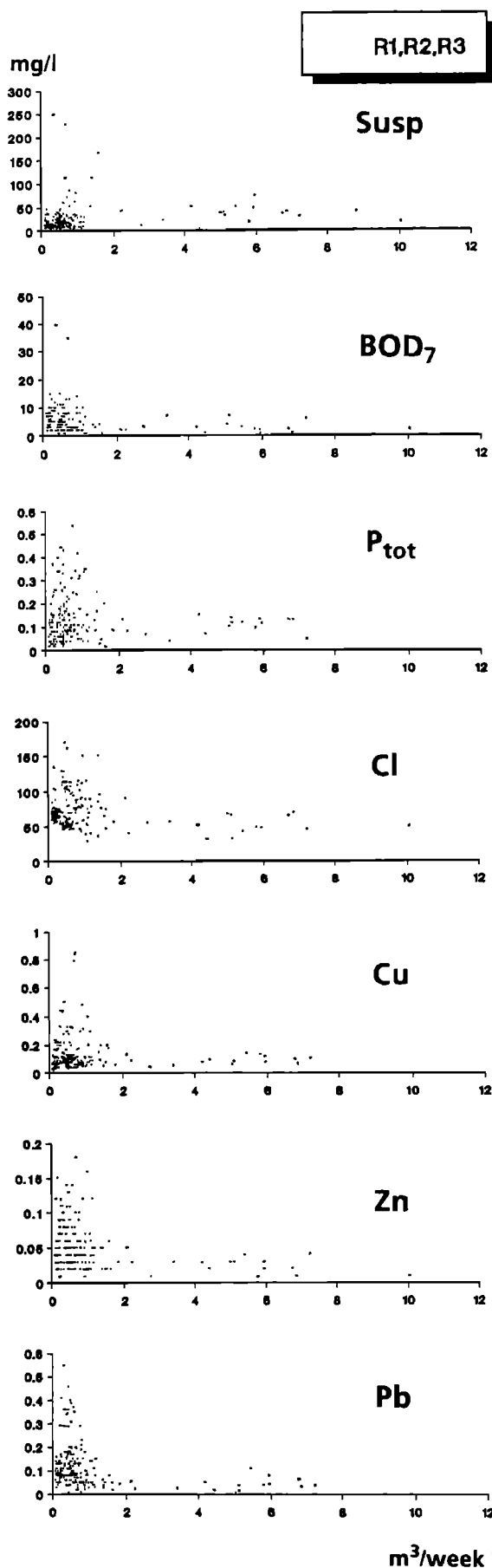
Fig 3. Relationship between stream water quality and stream discharge (R1, R2, and R3 stations; number of samples = 222).

lated heavy metals, six sediment samples were taken according to Figure 1 in August 1989. All samples were taken from the upper 5 cm of the sediments at places where flow rates were low and sedimentation was assumed to occur. Table 4 shows the results of the sediment analyses.

The different sediment samples displayed relatively homogeneous character regarding organic content, particle size distribution, general consistency, and color. The organic part (<10%) consisted mainly of root threads and fine material. The mineral part consisted mainly of clay minerals, quartz, and to a lesser extent, feldspar.

The metal concentrations show a considerable variation. However, all samples are considerably higher than the expected background values. The highest concentrations were found in the samples taken close to the storm water discharge points. The sediment samples subsequently verify that accumulation of heavy metals is occurring. However, the great variation in concentration shows that the areal distribution of accumulated heavy metals also is considerable.

Rivers are typical areas where processes of transportation dominate the bottom dynamics [Håkansson, 1984]. Thus the character of the sediments varies greatly (sand, twigs, silt, leaves, etc.). The limited number of sediment samples in the present study is not enough to give a reliable areal estimate of the heavy metal distribution for the entire river bottom. It may, however, be assumed that accumulation of heavy metals mainly takes place in regions of relatively low velocity [Wilber and Hunter, 1979]. The analyzed sediment samples display metal concentrations which are significantly higher than normally polluted sediments in transportation bottoms [Håkansson, 1984; Tada et al., 1983; Wilber and Hunter, 1979]. The mean concentrations of the sediment samples, however, are not large enough to explain the outcome of the mass balances. The extreme variation of the analyzed metal concentrations (Table 4) rather indicate that the bulk of the metals may accumulate in very localized places where the average velocity is small enough to allow for sedimentation.

ERRORS AND UNCERTAINTIES

Each component of the water budget estimation and mass transport calculation is associated with an error. Winter [1981] reports that probable error levels for water balance estimations are about 5% (stage-discharge relationships). However, the annual deviation in the water balance may be smaller because of long-term error compensation of independent, nonadditive measurement and estimation errors [Elder, 1985]. The initial annual water budgets indicated a net deficit of 9%. However, after correction for nonobserved snowmelt runoff, the maximum accumulated deficit decreased to less than 1%. This deficit of 1% is due mainly to nonpoint source inflow and outflow of groundwater from the reach. It appears therefore that the error in the water budget estimation does not significantly alter the results.

Errors associated with the water quality analyses differ depending on the water quality constituent. The metal analyses accuracy is depending on the detection limit but reported generally to be within ±10-20% (according to Swedish standards; see also APHA [1975]). However, since the concentrations usually were much higher than the detection limits, the accuracy is thought to be close to ±10%. For the
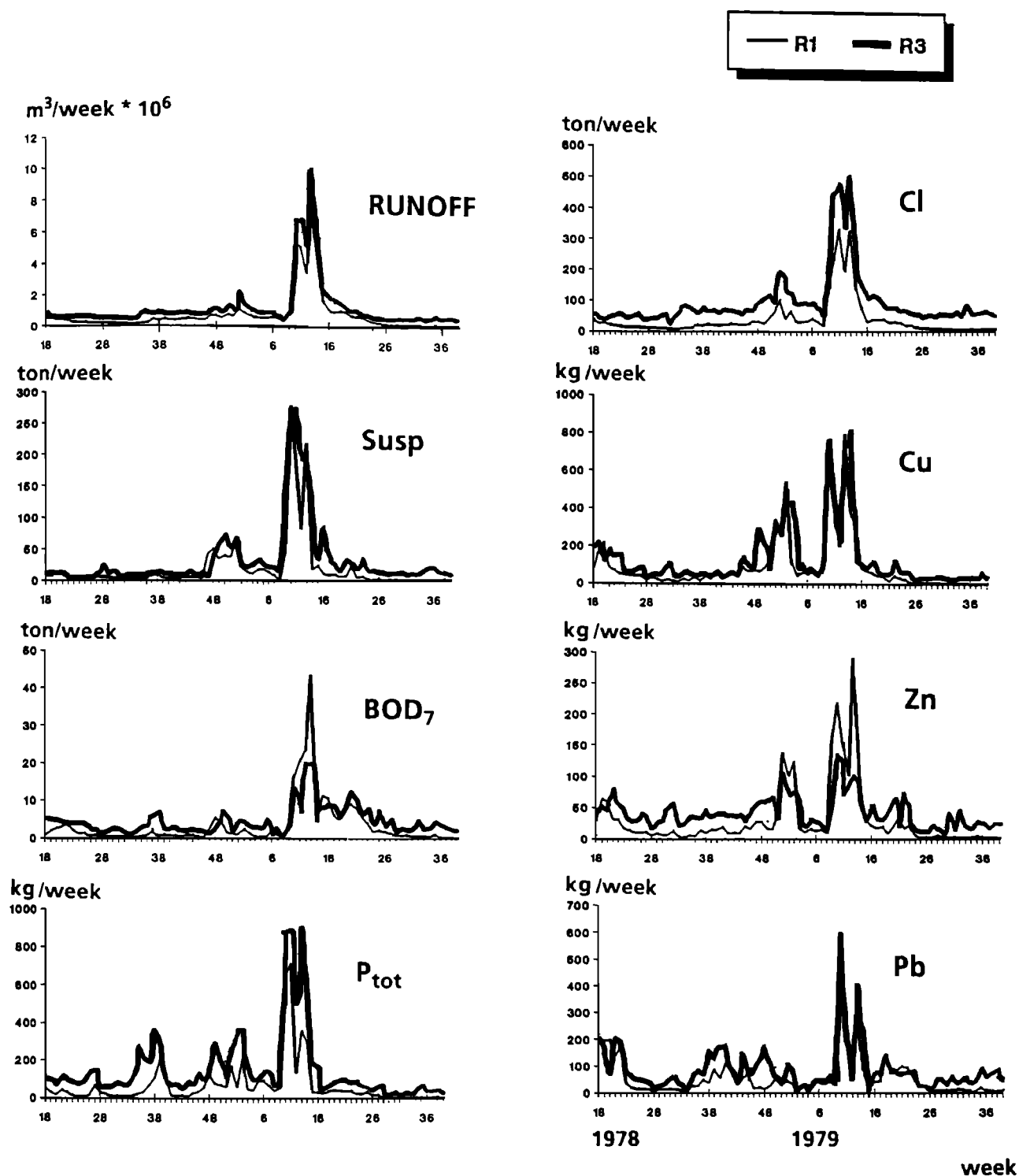
Fig 4. Water discharge and chemical mass transport at the inflow and outflow receiving water stations (R1 and R3 stations).

other water quality constituents, the analyses accuracy is estimated as suspended solids, ±20%; BOD_7, ±20%; P_{tot}, ±9%; and Cl, ±10% (according to Swedish standards and *APHA* [1975]). The analyses accuracy for these constituents is also dependent on the detection limits. However, since the analyzed concentrations in most cases were much greater than these limits, it is believed that the error in the analyses is smaller than the above mentioned accuracies.

Errors in water budgets and water quality analyses are carried over in the mass transport and mass budget calculations. Long-term error intervals were calculated according to *Winter* [1981], assuming that component errors are independent and nonadditive [*Mattraw and Elder*, 1984]. This showed that errors in the mass budgets are likely to be about 10%.

Chloride, which is often used as a natural tracer [*Bencala et al.*, 1987; *Feller and Kimmins*, 1979], displayed an accu-
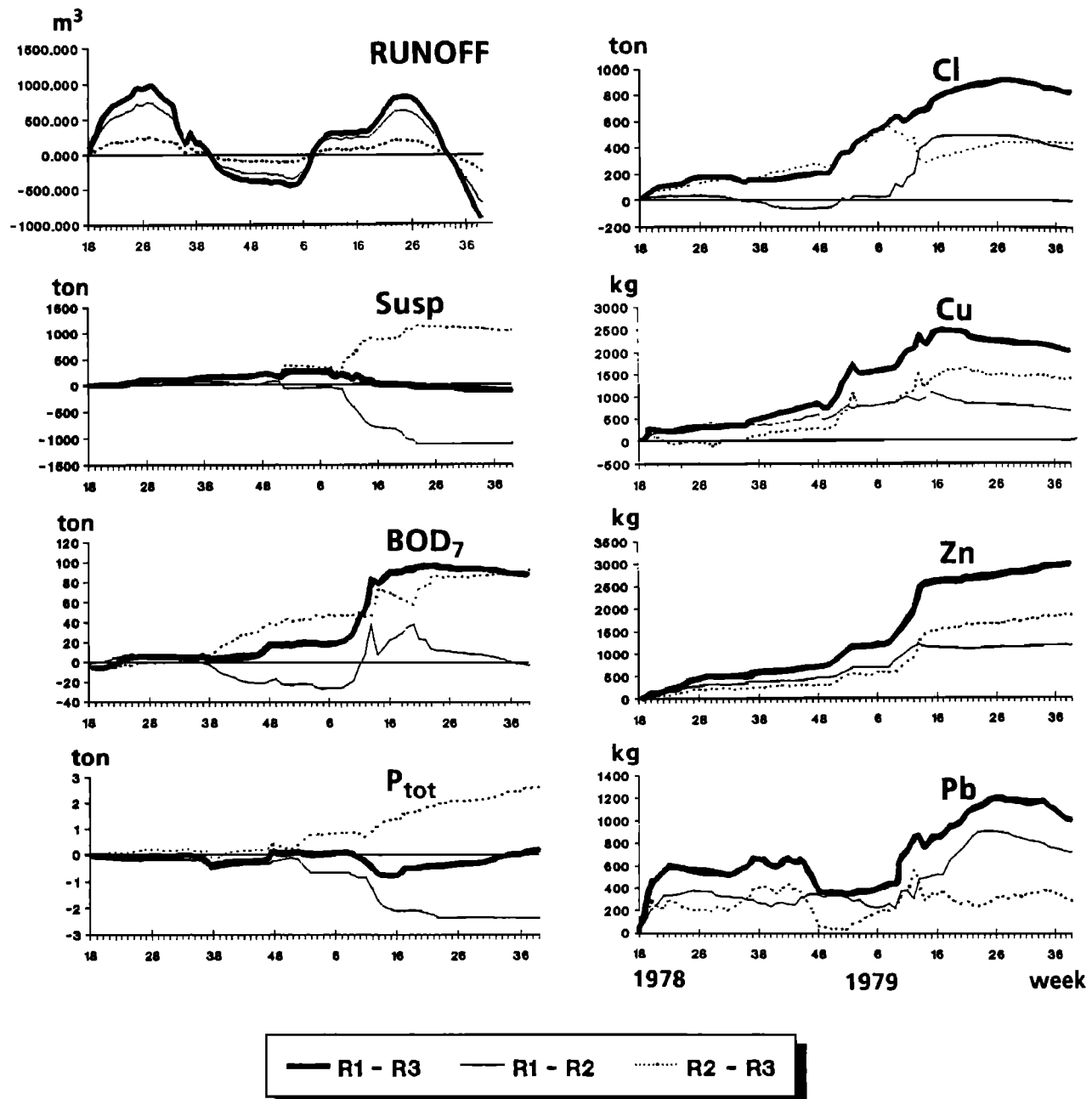
Fig 5. Accumulated surplus and deficit of water budgets and chemical mass balances at the inflow, intermediate, and outflow receiving water stations (R1, R2, and R3 stations).

mulation corresponding to 11% of the total mass inflow. This may indicate that errors equal about 11%. A number of studies, however, have shown that chloride may accumulate in watersheds [*Feller and Kimmins*, 1979; *Claridge*, 1970, 1975; *Schindler et al.*, 1976; *Likens et al.*, 1977]. Chloride concentrations and accumulation showed a pronounced seasonal trend (Figures 2 and 5). High concentrations during winter are caused by deicing practices on streets and impermeable surfaces. The peaks in concentration during the summer and autumn period may, however, be a result of chloride deposited in particulate form during the dry summer and wash-out by the autumn rains [*Juang and Johnson*, 1967; *Feller and Kimmins*, 1979].

TABLE 3. Accumulated Deviations of Chemical Mass Balances in Tons, Total (R1-R3) and Depending on Reach (R1-R2 and R2-R3) for the 17-Month Period

	R1-R3	R1-R2	R2-R3
SS	-100 (4%)	-1100	1000
BOD_7	90 (20%)	0	90
Cl	850 (11%)	400	450
P_{tot}	0 (0%)	-2.5	2.5
Cu	2.1 (19%)	0.7	1.4
Zn	3.2 (47%)	1.2	2.0
Pb	1.0 (14%)	0.7	0.3

The total accumulated deviation divided by the total influx to the reach is given in parentheses.

TABLE 4. Sediment Samples Taken From the Upper 5 cm of
Sediments During August 1989

	Cu	Zn	Pb
	62	270	180
	740	1700	75
	91	450	120
	66	310	50
	69	250	49
	52	200	35
Mean	180	530	85
Median	70	290	65
Standard deviation	615	1295	125
Background	20–40	70–120	10–30

Values are given in parts per million; background values were taken from *Wedepohl* [1969] and *National Swedish Environmental Protection Board* [1985].

The mass transport calculations are based on mixed weekly flow-proportional samples. This means that even if weekly data are used in the transport calculations, information on shorter processes is contained in the samples.

The winter in 1978/1979 was unusual with large amounts of snow. Therefore the winter may not be regarded as representative for conditions in south Sweden. Even so, the measurements during this year are giving interesting information on how pollutants may accumulate and transport during different seasons of the year on a typical transportation bottom. Since the winter was unusually cold with much snow during a long period, these months represent conditions favorable for pollutant accumulation (low discharge combined with high pollution concentrations). Similarly, the rapid snowmelt with high peak flows during a few weeks represent conditions when resuspension/winnowing/ transportation may be assumed [e.g., *Håkansson*, 1984]. This expected seasonal behavior was, however, not clearly seen in the accumulated chemical mass balances (Figure 5). The snowmelt with the resulting annual bulk mass transportation rather seemed to enhance the accumulation rates. In the same way, dry periods with low discharge in the river did not display any characteristic accumulation tendency. Consequently, it therefore seems as if pollutant retention in streams and river bottom dynamics are much more complicated than can be explained by just mechanical factors and simple discharge relationships.

SUMMARY AND DISCUSSION

The present study has showed than an essential pollution build-up seems to take place in stream sediments which receive urban and rural runoff. Mass budget calculations indicate that 90 bons of BOD_7, 850 tons of chloride, 2.1 tons of copper, 3.2 tons of zinc, and 1.0 ton of lead are retained in the sediments of the investigated stream over a 17-month period. Other pollutants such as suspended solids and phosphorus appear to be both retained and washed-out, depending on loading rates and local stream conditions. The retained pollutants represent a substantial part of the total mass transport through the stream (14–47%). Almost half of the transported zinc, is retained within the stream sediment. Subsequently, the deposited pollutants represent a potential source of pollution (however, also depending on their form and speciation).

The rather great sediment retention of various constitu-

ents is also indicated by the present river management plan for the River Höje. At present, dredging of bottom sediments at the investigated reach is needed every 4–5 years in order to avoid discharge capacity problems. This means that pollutants in the sediments may either be reallocated to deposits for dredged material (usually on top of the river banks) or may resuspend and be transported downstream (this depends on dredging technique and on the pollution form and speciation).

Large retention of pollutants to stream sediments, for example, heavy metals, also has been observed in other studies. *Imhoff et al.* [1980] found that about 31% of the total mass transport of heavy metals to the Ruhr drainage system are retained in the stream sediments.

The physical reasons for sediment retention can not be investigated in this study. However, it is expected that a number of different factors are interacting. Mechanical factors such as sedimentation and erosion may interact with chemical and biological activities (e.g., biodegradation and nutrient and microsubstance uptake by plants). The significant pollutant build-up during high flows indicates, however, that purely mechanical factors play a minor role. The heavy metals copper, zinc, and lead display different seasonal accumulation patterns. Copper and zinc show a more or less constant accumulation over the year similar to that of the suspended sediments (increased rates during snowmelt). Lead, on the other hand, shows a more periodic behavior similar to that of the accumulated deviations of the water balance. It seems therefore that lead is correlated to the outflow and inflow of water through the river bottom. Further sediment and water quality sampling is proposed in order to verify the results presented in this paper.

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